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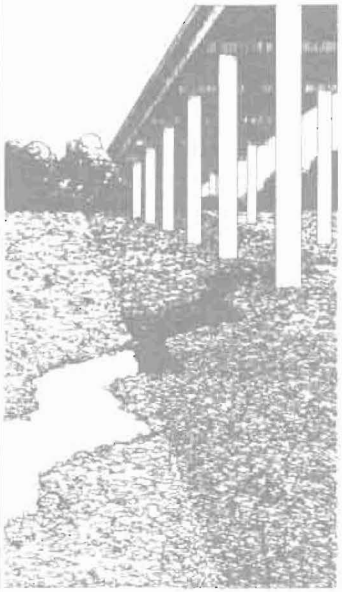

ENVIRONMENTAL LABORATORY

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TRICLOPYR (GARLON 3A) DISSIPATION IN LAKE SEMINOLE, GEORGIA

by

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A liquid formulation of triclopyr (Garlon 3A) was applied under Experimental Use Permit at proposed maximum rates to areas of Lake Seminole, GA, in order to examine herbicide dissipation and environmental fate. Residue persistence varied between the two treated plots. Triclopyr residues persisted in water above detectable levels through posttreatment day 3 in one plot and through posttreatment day 21 in the other. The residue half-life for the two plots was 0.5 and 3.4 days, respectively. Triclopyr (≤0.3 mg/kg) was found in the sediment only on treatment day and posttreatment day 1. Triclopyr residues in plant tissue (>1.0 mg/kg) existed through posttreatment day 8. Triclopyr residues were not detected in fish but were detected in caged crayfish through posttreatment day 21. Indigenous clam tissue contained triclopyr residues only through posttreatment day 1. Based on the results of this study, applications of the Garlon 3A formulation of triclopyr for submersed aquatic plant control should not produce adverse effects on the environment. However, further evaluation of the accumulation and effects of triclopyr on clams and crayfish should be considered before establishing tolerance limits.

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PREFACE

This study was conducted by personnel of the US Army Engineer Waterways Experiment Station (WES) as a part of the US Army Corps of Engineers Aquatic Plant Control Research Program (APCRP). Funds for the effort were provided by Headquarters, US Army Corps of Engineers (HQUSACE), under Department of the Army Appropriation No. 96X3122, Construction General 902740. Mr. E. Carl Brown, HQUSACE, was Technical Monitor.

The work was conducted under the general supervision of Dr. John Harrison, Chief, Environmental Laboratory (EL), Mr. Donald L. Robey, Chief, Ecosystem Research and Simulation Division (ERSD), EL, and under the direct supervision of Dr. Thomas L. Hart, Chief, Aquatic Processes and Effects Group (APEG), ERSD. Mr. J. Lewis Decell was Program Manager, APCRP. The study was planned and designed by Dr. Howard E. Westerdahl, APEG. Mr. W. Reed Green and Dr. Westerdahl conducted the study and prepared this report.

The project was conducted in cooperation with The Dow Chemical Company, Midland, MI. Dr. Kent B. Woodburn of The Dow Chemical Company provided technical assistance. Field assistance and technical support were provided by personnel from The Center for Aquatic Plants (CAP), University of Florida, Dr. Joseph C. Joyce, Director. Mr. Victor Ramey of CAP assisted in field sampling along with Mr. Kyle Betrand and Mses. Linda Nelson, Cindy Waddle, and Yvonne Vallette of APEG. Reviewers of this paper were Drs. Kurt Getsinger and Doug Gunnison of APEG. This report was edited by Mr. Bobby Odom, Information Technology Laboratory, working under the Intergovernmental Personnel Act.

Commander and Director of WES was COL Dwayne G. Lee, EN. Technical Director was Dr. Robert W. Whalin.

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CONTENTS

TRICLOPYR (GARLON 3A) DISSIPATION IN LAKE SEMINOLE, GEORGIA

PART I: INTRODUCTION

1. The development of new herbicide formulations for aquatic plant control is necessary to ensure that the most environmentally safe and effective chemistry is reflected in the products available for use by the Corps of Engineers (CE) and State and local agencies. Cooperative field investigations between the CE and industry have been encouraged. These operational field studies allow the CE to acquire environmental fate information which is not economically feasible to obtain independently. This information is used to develop specific guidance and use recommendations for the Department of Defense.

2. Getsinger and Westerdahl* is the only open publication at this date evaluating the use of triclopyr (Garlon 3A) as an aquatic herbicide. Based in part on the results of this research,* The DOW Chemical Company decided to perform the additional testing required for aquatic registration of this herbicide formulation. Company representatives requested our assistance in designing and conducting the necessary field testing, under the US Environmental Protection Agency (USEPA) Experimental Use Permit (EUP), to support the petition for aquatic registration. The results of these field tests will be used to establish safe and environmentally compatible application rates, allowable water residue levels in drinking water (AWRLDW), tolerances for fish and other nontarget organisms, and appropriate use restrictions.

Chemistry and Mode of Action

3. Garlon 3A is a liquid formulation of triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) (Figure 1) combined with a triethylamine salt. The formulation is 44 percent active ingredient (ai) and 31.8 percent acid equivalent (a.e.) (359 g/ℓ, 3 lb/gal). For consistency and clarity, triclopyr

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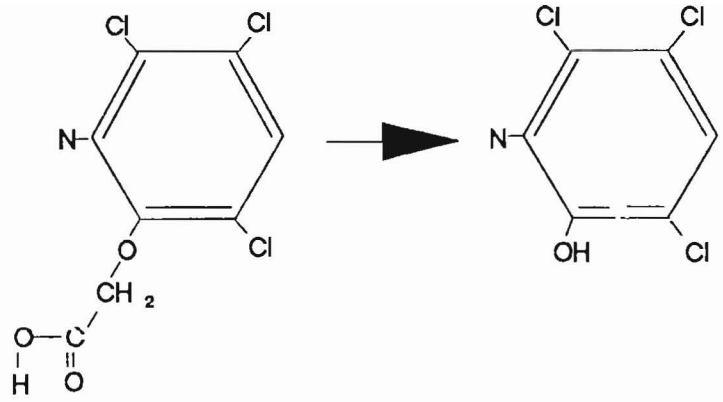
* K. D. Getsinger and H. E. Westerdahl. 1984. "Field Evaluation of Garlon 3A (Triclopyr) and 14-ACE-B (2,4-D BEE) for the Control of Eurasian Watermilfoil," Miscellaneous Paper A-84-5, US Army Engineer Waterways Experiment Station, Vicksburg, MS.



Triclopyr TCP

Figure 1. Triclopyr and its by-product TCP

concentrations reported in this report will be acid equivalents (a.e.). The major by-product of triclopyr is TCP (3,5,6-trichloro-2-pyridinol) (Figure 1). Triclopyr is hydrolyzed into TCP, both metabolically by plants and microflora and photochemically. Triclopyr is an auxin-type selective herbicide used currently for the control of many woody and herbaceous broadleaf plants.* Most grasses are tolerant to triclopyr. Pending review by USEPA of data collected under the EUP, triclopyr's registration will be broadened to include broadleaf weed and brush control along banks of canals, streams, and ditches, and for the control of waterhyacinth (*Eichhornia crassipes* (Mart.) Solms.) and Eurasian watermilfoil (*Myriophyllum spicatum* L.).

4. Triclopyr's uptake and mode of action are similar to that of phenoxy herbicides with accumulation of triclopyr concentrated in the meristematic regions. However, the exact physiological mechanism of action is not known. Uptake through the foliage and roots and movement of triclopyr within plants is greatest under conditions of warm temperatures and long photoperiods** when photosynthetic and meristematic activity is greatest.

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* Weed Science Society of America. 1983. Herbicide Handbook of the Weed Science Society of America, 5th ed., Champaign, IL.

** S. R. Radosevich and D. E. Bayer. 1979. "Effect of Temperature and Photoperiod on Triclopyr, Picloram and 2,4,5-T Translocation," Weed Science, Vol 27, pp 22-27.

Persistence and Environmental Fate

5. Physical, chemical, and biological processes affect triclopyr concentration and exposure time in the aquatic environment. Accumulation and metabolism of triclopyr by the treated plants and microflora are major factors influencing residue persistence in water. Photodegradation also influences residue dissipation. The half-life of triclopyr in water is predicted to be between 2 hr and 6 days, depending on water depth, time of year, and geographical location.* Hydrodynamic characteristics of the treated system also influence the concentration and exposure time of triclopyr and its degradation metabolite TCP. Water movement and exchange, along with diffusion gradients, will dilute and disperse residues accelerating dissipation. Reduction in residue retention time may be beneficial to nontarget organisms but may not provide the necessary exposure time to control the target plants.

6. Getsinger and Westerdahl** found that the persistence and dissipation of triclopyr in the aquatic environment were very short-lived. Triclopyr persistence in the water was less than 7 days following a low rate application of Garlon 3A (1.0 mg a.e./ℓ), while persistence was less than 14 days following a high rate application (2.5 mg a.e./ℓ). Triclopyr was found outside the treated areas (>50 m) from both applications. However, triclopyr residues were not detected in the sediment of either treated area throughout the study.

7. The direct and indirect effects of herbicide treatments in the aquatic environment, e.g., the relative toxicity of the chemical and its metabolites and dissolved oxygen depletion from decaying plants, on nontarget organisms should be minimized. Triclopyr has a low order of toxicity to wildlife and fish.† The 96-hr LC_{50} levels for bluegill and rainbow trout exposed to triclopyr under controlled laboratory conditions are 148 and 117 mg a.e./ℓ, respectively. These high levels of triclopyr would not be achieved in the treated water following application since the maximum concentration proposed for aquatic use is 2.5 mg a.e./ℓ. Toxicological information is not available

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* P. J. McCall and P. D. Gavit. 1986. "Aqueous Photolysis of Triclopyr and Its Butoxyethyl Ester and Calculated Environmental Photodecomposition Rates," Environmental Toxicology and Chemistry, Vol 5, pp 879-885.

** op. cit.

† Weed Science Society of America, op. cit.

on the effects of triclopyr on clams, crayfish, or other nontarget aquatic organisms.

Objectives

8. The objectives of this investigation were to examine the residue levels and evaluate dissipation of triclopyr and TCP residues in water, sediment, plants, fish, clams, and crayfish, resulting from operational treatment of submersed aquatic plants in Lake Seminole, Georgia, using Garlon 3A.

PART II: MATERIALS AND METHODS

Study Area

9. The study area consisted of three 4-ha areas containing Eurasian watermilfoil (*Myriophyllum spicatum* L.) and hydrilla (*Hydrilla verticillata* (L.f.) Royle) in the Spring Creek tributary of Lake Seminole, Georgia (Figure 2). The upstream plot (plot 1) was selected as the untreated reference. The middle or second plot was treated by helicopter, and the third plot was treated by surface injection from an airboat. Each plot contained five sampling stations (Figure 2), one in the center of each quadrant and one in the center of the plot. Sampling stations outside the plots were selected approximately 100 m from the center of the plot margins. A downstream sample station was established about 1.5 km downstream from plot 3. The distance between plot 1 and plot 2 was approximately 1.0 km; plot 2 and plot 3, 1.3 km; and plot 1 and plot 3, 2.0 km.

10. Vegetation in the three plots differed at the time of treatment. Plot 1 contained (visual estimate) 98 percent Eurasian watermilfoil and less than 1 percent hydrilla. Most of the surface area was covered with Eurasian watermilfoil interspersed with hydrilla. Plot 2 contained 95 percent hydrilla and only 4 percent Eurasian watermilfoil with approximately 75 percent of the surface area covered with plants. Plot 3 contained 50 percent Eurasian watermilfoil and 35 percent hydrilla. The remaining 15 percent of the flora was pondweed (*Potamogeton* sp.) and the alga chara (*Chara* sp.). Approximately 75 percent of the surface area of plot 3 was covered with plants.

Herbicide Application

11. Garlon 3A was applied on 9 July 1986 to plots 2 and 3 at a rate of 94 ℓ/ha (10 gal/acre), which was equivalent to 3.4 kg a.e./ha (3 lb a.e./acre). The theoretical triclopyr treatment concentration was 2.5 mg a.e./ℓ, based on the average plot depth of 1.2 m. This rate was the maximum concentration allowed by EUP guidelines and was based in part on the results of Getsinger and Westerdahl.* The previous authors found that triclopyr

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* op. cit.

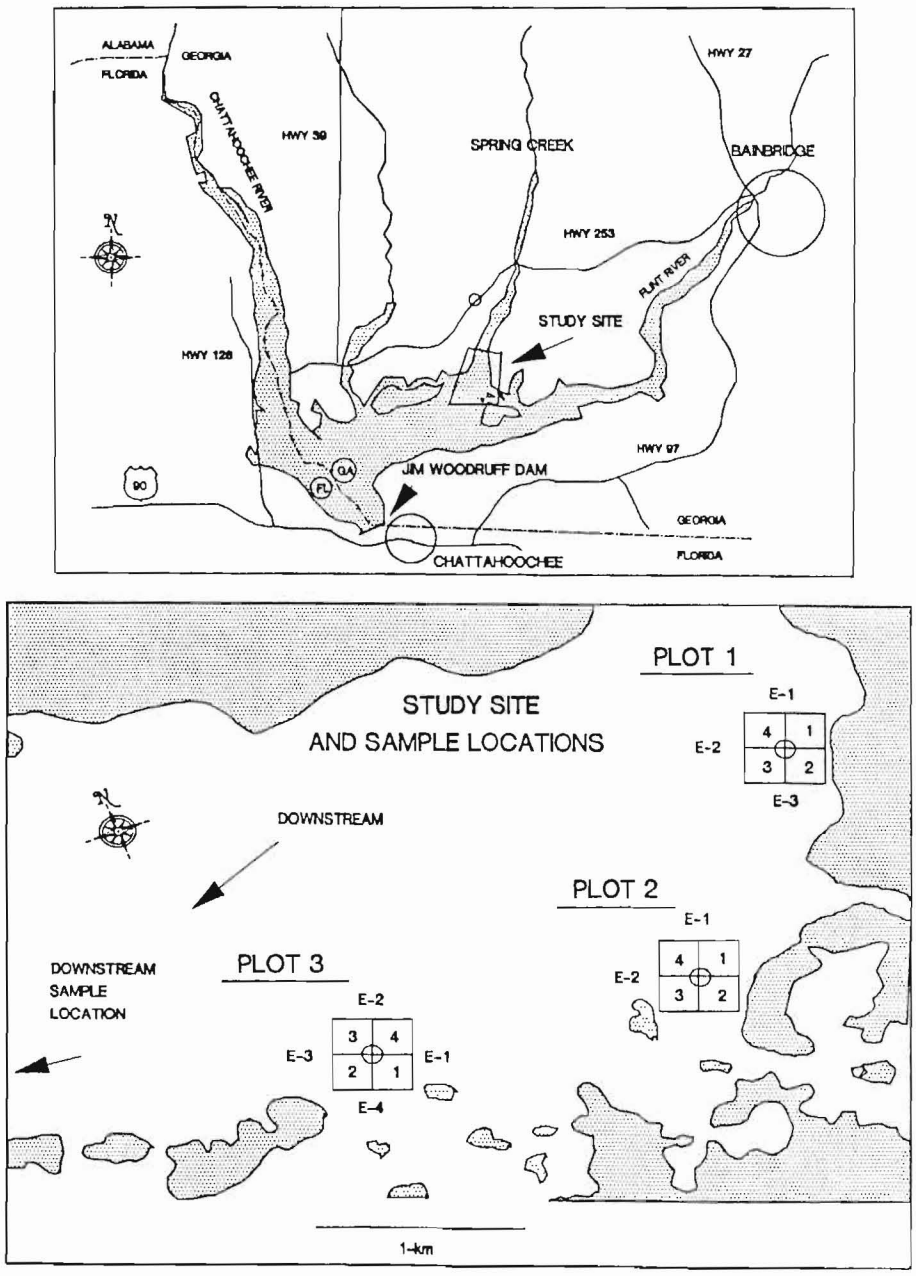

Figure 2. Study site and sample site locations with treatment plots enlarged to show detail

concentrations applied at this rate provided substantial Eurasian watermilfoil control. Garlon 3A was aerially sprayed, undiluted, to plot 2 with a Hughes 500 helicopter using a Simplex 5500 spray system. The equipment contained 32 raindrop nozzles on a 10-m boom. Half the nozzles were used, providing a spray pressure of 4.0 kg/cm^2 (20-22 psi) and a swath width of 7 m. The speed of the helicopter during application was 72 km/hr (45 mph).

Garlon 3A was applied, undiluted, to the third plot by surface injection using an operator constructed spray system mounted on an airboat. The equipment consisted of four nozzles providing a spray pressure of 703 kg/cm^2 (100 psi) and a swath width of 4 m. The speed of the airboat during application was 8 to 11 km/hr (5 to 7 mph).

Residue Sampling

12. Water, sediment, plants, fish, clams, and crayfish samples were placed on ice immediately after collection and stored frozen until triclopyr and TCP residues could be analyzed (Table 1). Water was collected using a 12-V d-c, centrifugal pump connected to a weighted drinking water quality garden hose with a screened intake. Water samples were obtained from two depths, approximately 0.3 m from the bottom and 0.3 m from the surface. In water 0.75 m deep or less, only a surface water sample was taken. Duplicate 1-ℓ water samples were obtained from the center of each quadrant, the center of the plot, each external site, and the downstream site.

13. Individual sediment samples were taken from the center of each quadrant and the center of the plot. Sediment surface samples (top 5-10 cm) were collected using a spring-loaded, trapdoor scoop (0.75-ℓ), connected to a 3-m-long by 3-cm-diam steel pipe. Several scoops of sediment were collected at each sample site and mixed in a stainless steel bowl to provide one 1-ℓ sample.

14. Plant samples (foliage) were collected using a garden rake and were composed of both hydrilla and Eurasian watermilfoil when available. The water was drained from the plant material before being placed in a bag. Individual plant samples were taken from the center of each quadrant and the center of the plot through posttreatment day 3. Subsequent plant samples taken from the quadrants were composited into one sample.

15. The nontarget organisms analyzed for residues included fish, clams, and crayfish. Fish were collected from each plot following electric shocking of the natural population. Individuals of the same taxa were combined into one sample and bagged. Fish samples were separated into nongame and game fish. Nongame fish included: brown bullhead, *Ictalurus nebulosus* (Lesueur); common carp, *Cyprinus carpio* Linnaeus; chain pickerel, *Esox niger* Lesueur; gizzard shad, *Dorosoma cepedianum* (Lesueur); lake chubsucker, *Erimyzon sucetta*

(Lacepede); and spotted sucker *Minytrema melanops* (Ratinesque). Game fish included: bluegill sunfish, *Lepomis macrochirus* Rafinesque; largemouth bass, *Micropterus salmoides* (Lacepede); redear sunfish, *Lepomis microlopus* (Gunther); warmouth sunfish, *Lepomis gluosus* (Cuvier); and yellow perch, *Perca flavescens* (Mitchill). Ten to fourteen clams (*Corbicula* sp.) were collected on each sampling date from the indigenous population in each plot. Due to the absence of an indigenous population in the treatment area, the crayfish (*Orconectes* sp.) were transferred from an outside population, and 40 to 45 individuals were placed in vinyl, open-mesh, polyvinyl chloride (PVC) pipe-framed cages, approximately 1.8 m^3. Two cages were anchored beneath the water surface, suspended off the bottom, near the center of each plot. The cages were partially filled with surrounding submersed vegetation, and small PVC pipe sections were placed in the cages to allow the crayfish a place to hide and minimize cannibalism. One to four crayfish were collected from each cage in the plot and placed into a 1-ℓ can.

Residue Analysis

16. Analyses of triclopyr and TCP residues were performed by The Dow Chemical Company. Sample preparation and analytical procedures followed Dow Chemical Methods and are summarized below.* All samples were analyzed using a Hewlett-Packard 5890 gas chromatograph, equipped with a ^{63}Ni electron-capture detector. Triclopyr and TCP residues reported in this report are net concentrations calculated by factoring gross concentrations measured by the percent recovery of the analytical procedure.

17. Water residue analysis followed Dow Chemical Method ACR 76.8.** The water was acidified, and residues were extracted with benzene. This aliquot was then methylated to form the TCP derivative and quantified for TCP. The aqueous solution with triclopyr was partitioned with diethyl ether and methylated to form the triclopyr methyl ester and quantified. These procedures provided an analytical validation limit of aqueous triclopyr and TCP of 0.01 and 0.05 mg/ℓ, respectively. Triclopyr levels between 0.005 and

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* Personal Communication, K. B. Woodburn, The Dow Chemical Company.
** Proprietary analytical procedures. Code number provided by Dow Chemical Co., Midland, MI.

0.010 mg/ℓ are considered to be <0.01 mg/ℓ, and levels <0.05 mg/ℓ are nondetectable. TCP levels between 0.025 and 0.050 mg/ℓ are considered to be <0.05 mg/ℓ, and levels <0.05 mg/ℓ are nondetectable. The average percent recoveries for aqueous triclopyr and TCP were 92 and 96, respectively.

18. Sediment residue analysis followed Dow Chemical Method ACR 84.2. Sediment samples were homogenized and gravity filtered to remove excess water. Triclopyr in the sediment was extracted with methanolic sodium hydroxide, acidified, saturated with salt, and partitioned into diethyl ether. The aliquot was then methylated to obtain the triclopyr methyl ester and quantified. TCP in the sediment was extracted similar to triclopyr. The sediment extract was partitioned into benzene and then sodium bicarbonate. The TCP aliquot was then methylated and quantified. These procedures provided an analytical validation limit of sediment-absorbed triclopyr and TCP of 0.10 and 0.05 mg/kg, respectively. Triclopyr levels between 0.05 and 0.10 mg/kg are considered to be <0.10 mg/kg, and levels <0.05 mg/kg are considered to be nondetectable. TCP levels between 0.025 and 0.050 mg/kg are considered to be <0.05 mg/kg, and levels <0.025 mg/kg are considered to be nondetectable. The average percent recovery for triclopyr and TCP residues in sediment was 84 and 88, respectively.

19. Plant residue analysis followed Dow Chemical Method ACR 77.4. Plant samples were drained of excess water and 10 g of plant material was extracted with methanolic sodium hydroxide over a filter and diluted with water. The plant material was then acidified and partitioned with diethyl ether/hexane. Triclopyr was then extracted with sodium bicarbonate, partitioned, methylated, and quantified. TCP was extracted from the aqueous-methanol filtrate, acidified, and partitioned with benzene. The aliquot was then methylated and quantified. These procedures provided an analytical validation limit of triclopyr and TCP in plants of 1.0 and 0.05 mg/kg, respectively. Triclopyr levels between 0.05 and 1.0 mg/kg are considered to be <1.0 mg/kg, and levels <0.05 mg/kg are considered to be nondetectable. TCP levels between 0.025 and 0.050 mg/kg are considered to be <0.05 mg/kg, and levels <0.025 mg/kg are considered to be nondetectable. The percent recovery for triclopyr and TCP residues in plants was 76 and 101, respectively.

20. Fish residue analysis followed Dow Chemical Method ACR 45I for triclopyr and ACR 70.19R for TCP. Fish were prepared for triclopyr analysis by extracting a 10-g portion of the homogenized edible fish material with

methanolic sodium hydroxide. The extract was then acidified, saturated with salt, and partitioned with diethyl ether/hexane. The organic phase was then partitioned with sodium bicarbonate, acidified, saturated with salt, and diluted with methanol. This aliquot was then repartitioned and methylated for quantification. Fish were prepared for TCP analysis by extracting a 10-g portion of homogenized fish material with methanol. This material was then back extracted with benzene, acidified, saturated with salt, and methylated for quantification. These procedures provided an analytical validation limit for triclopyr and TCP in fish of 0.10 and 0.05 mg/kg, respectively. Triclopyr levels between 0.05 and 0.10 mg/kg are considered to be <0.10 mg/kg, and levels <0.05 mg/kg are considered to be nondetectable. TCP levels between 0.025 and 0.050 mg/kg are considered to be <0.05 mg/kg, and levels <0.025 mg/kg are considered to be nondetectable. The average percent recovery for triclopyr and TCP residues in fish was 73 and 70, respectively.

21. Clam and crayfish residue analysis followed Dow Chemical Method ACR 77.4SI. Whole crayfish and clam muscle were homogenized. One-gram portions were extracted with methanolic sodium hydroxide, acidified, saturated with salt, and partitioned with sodium bicarbonate. This phase was then repartitioned with benzene, methylated, and quantified for TCP. The benzene phase was partitioned again for triclopyr analysis with diethyl ether and methylated for quantification. These procedures provided an analytical validation limit for triclopyr and TCP in crayfish and clams of 0.10 and 0.05 mg/kg, respectively. Triclopyr levels between 0.05 and 0.10 mg/kg are considered to be <0.10 mg/kg and levels <0.05 mg/kg are considered to be nondetectable. TCP levels between 0.025 and 0.050 mg/kg are considered to be <0.05 mg/kg, and levels <0.025 mg/kg are considered to be nondetectable. An average 82 percent recovery was obtained for both triclopyr and TCP residues in crayfish and clams.

Water Quality

22. Water quality (temperature (T), pH, specific conductance, and dissolved oxygen (DO)) was monitored pretreatment through posttreatment day 21 in all three plots. Two Hydrolab^{tm} Datasonde I^{tm} programmable, submersible monitoring units were placed near the center of each plot, one approximately 0.3 m from the bottom and one approximately 0.3 m from the water surface. The units

were programmed to take measurements every 0.5 hr. The Datasonde^{tm} units were removed from the water every 4 to 7 days for data retrieval and recalibration prior to being returned to the plots. Specific conductance was standardized for T where raw conductivity × F(T) = compensated conductivity:

$$F(T) = 1 + 0.028(T - 25) + 108.2(10^{-6})(T - 25)^2 \quad (1)$$

Dissolved oxygen was corrected for conductivity (C) at T where raw DO × F(C) = true DO:

$$F(C) = 1 - C\left[3.439(10^{-3}) + \frac{0.316}{(22.1 + T)^2}\right] \quad (2)$$

PART III: RESULTS AND DISCUSSION

Triclopyr and TCP Residues

Water

23. The dissipation and persistence of triclopyr residues in water varied among the two treated plots (Tables 2-3). The initial triclopyr concentrations (0 days after treatment) from the two treated plots were close to the expected concentration of the application (2.5 mg/ℓ). Triclopyr residues persisted through posttreatment day 21 in plot 2 and through day 3 in plot 3 (Figure 3). The triclopyr first-order half-life in the surface and

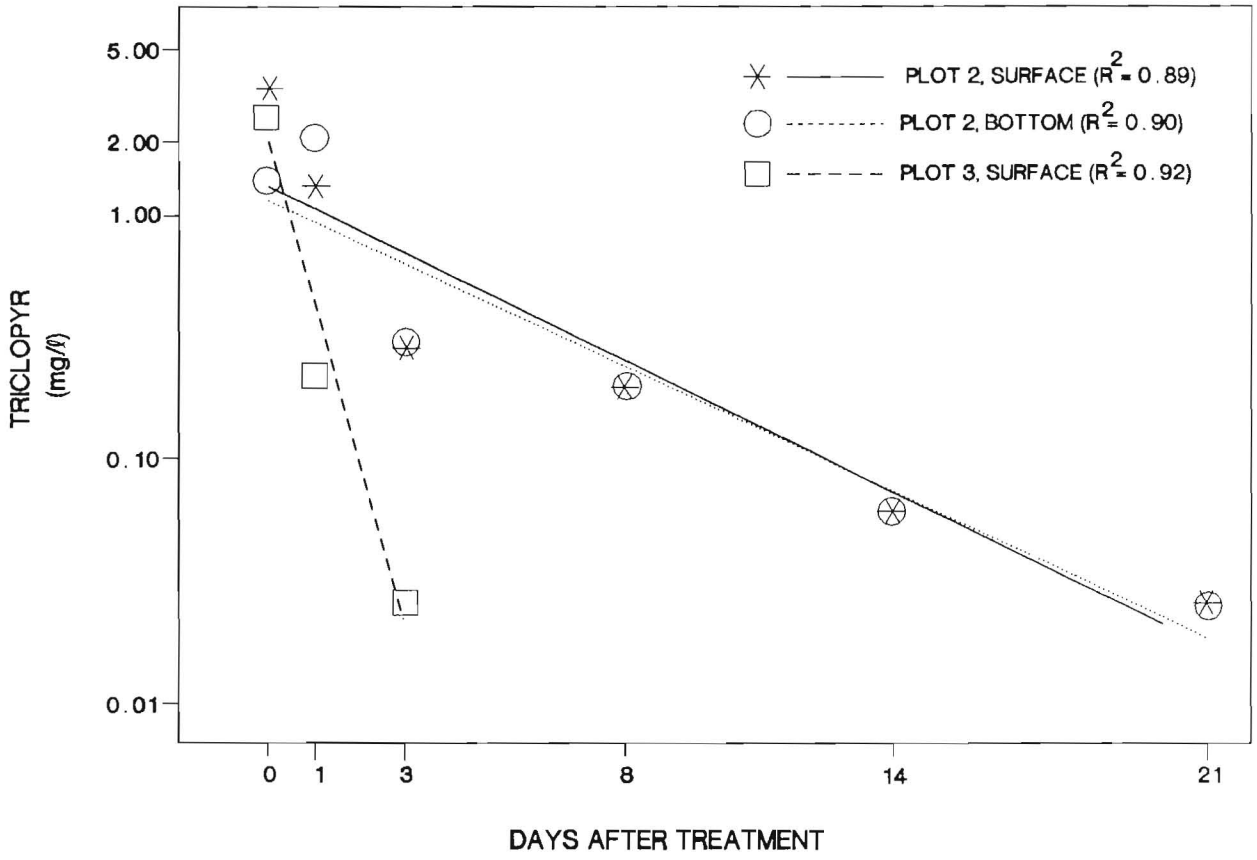

Figure 3. Triclopyr dissipation in the two treated plots where lines are first-order estimates using sample means collected from the five internal sample sites

bottom water of plot 2 was 3.3 and 3.5 days, respectively, and 0.5 day in the surface water of plot 3. Similar results were observed with triclopyr by Getsinger and Westerdahl.*

24. Triclopyr residues were detected in very few water samples collected from the reference plots (Tables 2-3). The barely detectable residue level on posttreatment day 0 in the reference plot (plot 1) was probably caused by sample contamination. However, detectable concentrations of triclopyr on days 8 and 14 were probably caused by the movement of water along the shore, north from plot 2 to plot 1. The prevailing winds were from the southwest, and the surface currents would travel north along the shoreline.

25. Triclopyr residues in the water collected from the external sampling sites reflected those levels found inside the plots after the day of treatment (Table 3). Residues persisted outside of plot 2 through posttreatment day 21. All samples collected from the external sites of plot 3 contained residues through posttreatment day 3, and two samples contained triclopyr at posttreatment day 8. Triclopyr residues were not detected in any of the samples collected from the downstream sample site.

26. Detectable TCP concentrations were found only in water samples collected from plots 2 and 3 (Table 4). In plot 2, detectable levels of TCP were detected in the surface and bottom samples of quadrant 2 on the day of treatment and again in the surface sample on posttreatment day 1. TCP was not detected in the remaining water samples. Both the surface and bottom water samples from plot 3, collected from one sample site on the day of treatment, contained TCP. The remaining water samples were void of detectable levels of TCP. No water samples collected outside the three plots and the downstream sample site contained detectable levels of TCP.

27. These results demonstrate the residue persistence and dissipation variability that can occur among treated areas even within the same body of water. The more rapid dissipation of triclopyr residues in the water from plot 3, than in plot 2, was probably a result of a number of interacting factors, e.g., water movement and degradation of triclopyr through photolysis. Examination of these factors was beyond the limits of this study; however, the possible influence that these factors had on residue persistence should be

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* op. cit.

noted. Water movement was probably a major factor influencing residue dissipation. Plot 2 was protected on two sides by land and was 2 to 3 km from the main channel of the tributary arm; plot 3 was virtually open on all sides and was less than 1 km from the main channel. Water currents originating from upstream along with wind-generated mixing patterns could have dispersed and dissipated the residues quicker in plot 3 than in plot 2.

28. Vegetative plot cover at the time of treatment may have also influenced the photodegradation of triclopyr. The hydrilla canopy in plot 2 covered 75 percent of the water surface. Close to 35 percent of plot 3 was open, not covered with vegetation. Photolysis of triclopyr may have occurred more rapidly in plot 3 since the water column was more open, and the depth was less than in plot 2. Exposure of triclopyr to summer sunlight in surface water located at the latitude where this study was conducted was predicted to produce a residue half-life of about 2 hr.*

Sediment

29. Triclopyr accumulation and persistence in the sediment was short-lived (Table 5). Triclopyr residues from the liquid formulation generally reside in the water column and do not accumulate in the sediment.* Small quantities (>0.10 to 0.64 mg/kg) of triclopyr were found in sediment initially after treatment. However, residues were at, or below, the analytical detection limit by posttreatment day 1 and remained below detection throughout the remainder of the study. Triclopyr residues were not detected in any sediment samples collected from the reference plot (plot 1) during the study. TCP residues were not detected in any sediment samples from all three plots throughout the study.

30. Since residues do not persist in the sediment, there should be little, if any, effect on nontarget benthic organisms as indicated by the clam data. The residues detected in the crayfish described later may have been unrealistically high. These crayfish were artificially maintained in cages, suspended in the water column, and not allowed to burrow into the sediment and avoid triclopyr exposure. Additionally, since crayfish are omnivorous, they may have ingested the triclopyr while feeding on treated vegetation within the cages.

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* McCall and Gavit, op. cit.

Plants

31. Triclopyr accumulated in the treated submersed aquatic plants and persisted through posttreatment day 8. Residue levels were highest initially after treatment (Table 6). TCP residue levels were low to nondetectable through posttreatment day 1 and were below analytical detection through the remainder of the study. These results suggest rapid breakdown and metabolism of triclopyr by the plants, and there appears to be no potential for residue release from the decaying plants into the surrounding environment.

Fish

32. Triclopyr residues were not detected over the analytical validation limit in any of the edible flesh from game and nongame fish collected during the entire study (Table 7). TCP was detected in small quantities in only five fish collected during the study. Based on these results, no adverse effects on the fishery would be expected when triclopyr is applied as spot treatments in a large water body.

Clams and crayfish

33. Triclopyr and TCP accumulation and persistence were greater in crayfish than the other compartments. Triclopyr residues were consistently higher in the crayfish collected from plot 2 than plot 3, and residues remained within the tissue through 21 days after treatment (Table 8). The hepato-pancreas organ (a primitive liver) of crayfish may concentrate the herbicide,* thereby, not reflecting what the levels would be in the edible flesh (tail). TCP residues in crayfish were low to nondetectable through the study. The potential adverse effect of triclopyr accumulation by crayfish is not understood at this time. Triclopyr residues in clam tissue were also greater in plot 2 samples than plot 3. However, residues were at, or below, detection by day 8 and remained below detection for the remainder of the study.

Water Quality

34. Water quality varied little between the untreated plot and the two treated plots (Table 9). Conductivity, dissolved oxygen, pH, and water

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* Personal Communication, K. B. Woodburn, The Dow Chemical Company.

temperature exhibited diel patterns over the 22-day measurement period (Appendix A).

35. The influence of plant decay on dissolved oxygen was the major water quality concern. As previously discussed, there was very little Eurasian watermilfoil in plot 2, and plot 3 contained only about 38 percent Eurasian watermilfoil. Therefore, the potential for large stands of decomposing vegetation was limited. The plant decay that did occur in the treated plots did not alter the DO concentrations. These results suggest that the herbicide treatments did not influence DO concentrations within the treated areas. Results might differ if large areas of homogeneous stands of Eurasian watermilfoil were treated.

PART IV: CONCLUSIONS AND RECOMMENDATIONS

36. Examination of triclopyr and TCP residue dissipation following Garlon 3A treatment at the prescribed rates should not produce adverse effects on the aquatic environment. The results showed that detectable triclopyr levels in water were variable (3-21 days), with residue half-life being less than 4 days. Residue accumulation in sediment, plants, and fish was negligible. TCP concentrations and persistence were transitory. However, the results of the crayfish evaluation indicate prolonged persistence of triclopyr and TCP. Further evaluation of triclopyr and TCP accumulation in clams and crayfish, separating the edible parts of the crayfish from the nonedible parts, must be accomplished before a tolerance level can be established.

Table 1

Sampling Schedule for Triclopyr and TCP Residues

Treatment Day	Water	Sediment	Plants	Fish	Crayfish	Clams
-1	X	X	X	X	X	X
0(4 hr)	X	X	X		X	X
1	X	X	X	X	X	X
3	X	X	X			
8	X	X	X	X	X	X
12				X		
14	X	X	X	X*	X	X
21	X	X	X	X	X	X
42	X	X	X			

* Plot 3 only.

Table 2

Average Triclopyr Residues (mg/ℓ) in Water, Inside the Plots

Location		Treatment Day -1	0	1	3	8	14	21	42
Plot 1									
Surface	Avg.	ND	0.01*	ND	ND	0.03	0.004	ND	ND
	S.E.	--	0.01	--	--	0.02	0.002	--	--
	N	5	5	5	5	5	5	5	5
Bottom	Avg.	ND	ND	ND	ND	0.01	0.01	ND	ND
	S.E.	--	--	--	--	0.003	0.003	--	--
	N	5	3	2	4	4	3	3	3
Plot 2									
Surface	Avg.	ND	3.16	1.32	0.28	0.18	0.06	0.03	ND
	S.E.	--	0.63	0.35	0.06	0.03	0.002	0.001	--
	N	5	5	5	5	5	5	5	5
Bottom	Avg.	ND	1.35	2.04	0.29	0.19	0.06	0.03	ND
	S.E.	--	0.55	0.40	0.08	0.01	0.006	0.001	--
	N	4	3	2	4	3	3	3	3
Plot 3									
Surface	Avg.	ND	2.54	0.22	0.03	ND	ND	ND	ND
	S.E.	--	0.43	0.09	0.008	--	--	--	--
	N	5	5	5	5	5	5	5	5

* Only one of five samples with detectable concentration (0.06 mg/ℓ) (see Table 1). Avg. = sample mean. S.E. = standard error of the mean. N = number of samples. ND = nondetectable.

Table 3

Triclopyr Residues (mg/ℓ) in Water

Location*			Treatment Day							
			-1	0	1	3	8	14	21	42
Plot 1	Q-1	S	ND	0.06	ND	ND	0.01	<0.01	ND	ND
	Q-2	S	ND	ND	ND		0.14	0.01	ND	ND
	Q-2	B	X	X	X		0.01	X	X	X
	Q-3	S	ND	ND	ND		ND	<0.01	ND	ND
	Q-3	B			X		ND	<0.01		
	Q-4	S			ND		<0.01	<0.01		
	Q-4	B					0.01	0.01		
	CTR	S					0.01	0.01		
	CTR	B					<0.01	0.01		
	E-1	S	X				ND	ND		
	E-1	B	X	X			ND	X	X	X
	E-2	S	X	ND			ND	ND	ND	ND
	E-2	B	X	ND			<0.01	<0.01	ND	ND
	E-3	S	X	ND			0.03	0.01	<0.01	ND
	E-3	B	X	ND			0.02	0.02	<0.01	ND
Plot 2	Q-1	S	ND	4.25	1.40	0.29	0.22	0.06	0.02	ND
	Q-1	B		0.69	1.47	0.58	0.21	0.06	0.03	
	Q-2	S		5.32	2.69	0.52	0.17	0.07	0.02	
	Q-2	B		0.66	2.61	0.22	0.19	0.05	0.03	
	Q-3	S		1.57	0.27	0.22	0.23	0.07	0.03	
	Q-3	B		2.70	X	0.18	0.16	0.07	0.02	
	Q-4	S		2.20	1.07	0.26	0.10	0.05	0.02	
	CTR	S		2.48	1.16	X	0.13	0.06	0.03	
	E-1	S	X	1.09	0.63	0.14	0.16	0.05	0.02	
	E-1	B	X	0.17	0.51	0.17	0.19	0.08	0.03	
	E-2	S	X	0.02	0.42	0.15	0.13	0.05	0.01	
	E-2	B	X	X	0.05	0.20	0.13	0.05	0.01	
Plot 3	Q-1	S	ND	3.41	0.62	0.16	ND	ND	ND	ND
	Q-2	S		1.39	0.16	ND	ND	ND	ND	ND
	Q-3	S		1.73	0.05	0.04	ND	ND	ND	ND
	Q-4	S		3.89	0.07	0.02	ND	ND	ND	ND
	Q-4	B		8.75	X	X	X	X	X	X
	CTR	S		2.27	0.2	0.05	<0.01	ND	ND	ND
	E-1	S	X	2.94	1.00	0.02	0.13	ND	ND	ND
	E-2	S	X	2.60	0.09	0.11	<0.01	ND	ND	ND
	E-2	B	X	2.43	0.32	0.03	0.01	X	X	X
	E-3	S	X	ND	<0.01	0.04	<0.01	ND	ND	ND
	E-3	B	X	ND	0.03	X	X	X	X	X
	E-4	S	X	X	0.41	0.01	<0.01	ND	ND	ND

* Q = quadrant site; CTR = center site; E = external site; S = surface sample; B = bottom sample; ND = nondetectable; X = no sample.

Table 4

TCP Residues (mg/ℓ) in Water

Location*			Treatment Day							
			-1	0	1	3	8	14	21	42
Plot 1			All samples nondetectable							
Plot 2	Q-1	S	ND	<0.05	<0.05	ND	ND	ND	ND	ND
	Q-1	B		<0.05	ND					
	Q-2	S		0.08	0.05					
	Q-2	B		0.06	ND					
	Q-3	S		<0.05	ND					
	Q-3	B		<0.05	X					
	Q-4	S		ND	<0.05					
	CTR	S		<0.05	ND	X				
	E-1	S	X	<0.05		ND				
	E-1	B		ND						
	E-2	S		ND				<0.50		
	E-2	B		X				ND		
Plot 3	Q-1	S	ND	0.05	ND	ND	ND	ND	ND	ND
	Q-2	S		<0.05						
	Q-3	S		<0.05						
	Q-4	S		0.07						
	Q-4	B		0.14		X	X	X	X	X
	CTR	S		<0.05		ND	ND	ND	ND	ND
	E-1	S	X	0.05				ND	ND	ND
	E-2	S		<0.05				ND	ND	ND
	E-2	B		ND				X	X	X
	E-3	S		ND				ND	ND	ND
	E-3	B		ND		X	X	X	X	X
	E-4	S		X		ND	ND	ND	ND	ND
Downstream		S	X	ND	ND	ND	ND	ND	ND	ND
		B	X	ND	ND	ND	ND	ND	ND	ND

* Q = quadrant site; CTR = center site; E = external site; S = surface sample; B = bottom sample; ND = nondetectable; X = no sample.

Table 5

Triclopyr and TCP Residues (mg/kg) in Sediment

Location*		Triclopyr/ TCP	Treatment Day -1	0	1	3	8	14	21	42
Plot 1		Tri	All triclopyr samples below detection.							
		TCP	All TCP sample below detection.							
Plot 2	Q-1	Tri	ND	<0.10	<0.10	ND	ND	ND	All	
		TCP		ND	ND	ND			subsequent	
	Q-2	Tri		0.18	X	<0.10			samples	
		TCP		ND	ND	ND			below	
	Q-3	Tri		0.31	ND	ND			detection.	
		TCP		ND	ND	ND				
	Q-4	Tri		0.21	0.10	<0.10				
		TCP		ND	ND	ND				
	CTR	Tri		0.23	ND	ND				
		TCP		ND	ND	ND				
Plot 3	Q-1	Tri	ND	0.10	<0.10	ND	ND	ND	All	
		TCP		ND	ND				subsequent	
	Q-2	Tri		<0.10					samples	
		TCP		ND					below	
	Q-3	Tri		0.11					detection.	
		TCP		ND						
	Q-4	Tri		0.64						
		TCP		ND						
	CTR	Tri		0.23						
		TCP		ND						

* Q = quadrant site; CTR = center site; ND = nondetectable; X = no sample.

Table 6

Triclopyr and TCP Residues (mg/kg) in Plants

Location*		Triclopyr/ TCP	Treatment Day -1	0	1	3	8	14	21	42
Plot 1	Q-1	Tri	ND	ND	ND	ND	All quadrant			
		TCP					samples were			
	Q-2	Tri					composited after			
		TCP					day 3 and are			
	Q-3	Tri		1.12			reported in Q-4.			
		TCP		ND						
	Q-4	Tri					ND	ND	ND	ND
		TCP								
	CTR	Tri								
		TCP								
Plot 2	Q-1	Tri	ND	5.66	2.55	1.10	All quadrant			
		TCP		ND	ND	ND	samples were			
	Q-2	Tri		6.15	2.93	2.11	composited after			
		TCP		ND	ND	<0.05	day 3 and are			
	Q-3	Tri		10.47	<1.00	1.27	reported in Q-4.			
		TCP		<0.05	ND	ND				
	Q-4	Tri		1.13	<1.00	X	1.10	ND	ND	ND
		TCP		ND	ND	X	ND			
	CTR	Tri		5.31	2.13	ND	1.09			
		TCP		<0.05	ND	ND	ND			
Plot 3	Q-1	Tri	ND	1.94	1.57	<1.00	All quadrant			
		TCP		ND	ND	ND	samples were			
	Q-2	Tri		1.55	ND	<1.00	composited after			
		TCP		ND	0.06	ND	day 3 and are			
	Q-3	Tri		1.63	ND	X	reported in Q-4.			
		TCP		ND	ND	X				
	Q-4	Tri		6.54	1.85	1.73	ND	ND	ND	ND
		TCP		<0.05	ND	ND				
	CTR	Tri		4.98	4.23	2.81				
		TCP		ND	ND	ND				

* Q = quadrant site; CTR = center site; ND = nondetectable; X = no sample.

Table 7

Triclopyr and TCP Residues (mg/kg) in Fish

Location	Type*	Triclopyr/ TCP	Treatment Day -1	1	8	12	14	21
Plot 1								
Nongame	SS	Tri	ND	ND	X	ND	X	X
		TCP		ND		0.05		
	CP	Tri		X		X		
		TCP				X		
	GS	Tri			ND	ND		
		TCP			ND			
	BB	Tri			X			
		TCP						
	LC	Tri	X			X		ND
		TCP	X			X		<0.05
Game	LB	Tri	ND	ND	ND	ND	X	ND
		TCP		ND	ND			ND
	WM	Tri		X	X			X
		TCP		X	X			X
	RE	Tri		ND	ND			ND
		TCP			ND	0.06		
	BG	Tri			X	ND		
		TCP				ND		
	YP	Tri		X		X		
		TCP		X		X		
Plot 2								
Nongame	CP	Tri	ND	X	X	X	X	X
		TCP		X	X	X		X
	GS	Tri		ND	<0.10	ND		ND
		TCP		ND	ND	ND		ND
	SS	Tri		X	X	X		X
		TCP		X				X
	LC	Tri	X	ND				ND
		TCP		ND				<0.05
	BB	Tri		X				X
		TCP		X				ND
Game	LB	Tri	ND	ND	ND	ND	X	ND
		TCP		ND	ND			<0.05
	RE	Tri		<0.10	ND			ND
		TCP		ND	0.07			0.15
	BG	Tri		<0.10	ND			X
		TCP		0.07	ND			X

(Continued)

* Nongame fish include: BB - brown bullhead, CC - common carp, CP - chain pickerel, GS - gizzard shad, LC - lake chubsucker, and SS - spotted sucker. Game fish include: BG - bluegill sunfish, LB - largemouth bass, RE - redear sunfish, WM - warmouth sunfish, and YP - yellow perch.

Table 7 (Concluded)

Location	Type	Triclopyr/ TCP	Treatment Day -1	1	8	12	14	21
Game (Cont)	YP	Tri	ND	ND	X	X	X	X
		TCP	ND	ND	↓	↓	↓	X
	WM	Tri	X	X	↓	↓	↓	ND
		TCP	X	X	↓	↓	↓	ND
Plot 3								
Nongame	CP	Tri	ND	X	X	X	X	X
		TCP	↓	X	↓	↓	X	X
	BB	Tri	↓	<0.10	↓	↓	ND	ND
		TCP	↓	<0.05	↓	↓	ND	ND
	CC	Tri	↓	X	↓	↓	X	X
		TCP	↓	X	↓	↓	↓	↓
	SS	Tri	X	ND	ND	↓	↓	↓
		TCP	X	ND	ND	↓	↓	↓
	GS	Tri	X	X	X	↓	↓	ND
		TCP	X	X	X	↓	↓	ND
Game	LB	Tri	ND	ND	ND	X	ND	ND
		TCP	↓	↓	↓	↓	ND	↓
	RE	Tri	↓	↓	↓	↓	ND	↓
		TCP	↓	↓	↓	↓	<0.05	↓
	BG	Tri	↓	↓	↓	↓	X	X
		TCP	↓	↓	<0.05	↓	X	↓
	WM	Tri	X	X	X	↓	ND	↓
		TCP	X	X	X	↓	ND	↓

Table 8

Triclopyr and TCP Residues (mg/kg) in Clams and Crayfish

Location	Sample	Triclopyr/ TCP	Treatment Day -1	0	1	8	14	21
Plot 1	Clam	Tri	ND	<0.10	ND	<0.10	ND	ND
		TCP		ND	ND	ND	ND	
	Crayfish	Tri		ND	ND	ND	ND	
		TCP		ND	0.05	0.06	0.06	
Plot 2	Clam	Tri	ND	2.49	3.44	<0.10	ND	ND
		TCP		<0.05	0.06	ND	ND	ND
	Crayfish	Tri		4.87	1.86	0.76	1.26	0.30
		TCP		0.07	0.19	0.21	0.49	<0.05
Plot 3	Clam	Tri	ND	0.77	0.24	ND	ND	ND
		TCP		ND	ND	ND	ND	ND
	Crayfish	Tri		0.25	0.59	0.20	0.14	0.18
		TCP		<0.05	0.07	0.10	ND	ND

Table 9

Water Quality Ranges and Averages from 1 Day Prior to Treatment Through 21 Days After Treatment

Location Plot*	Conductivity µmho/cm		Dissolved O_2 mg/ℓ		pH		Temperature °C	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
1-S	76-124	93	2.05-11.93	6.98	7.91-9.51	8.81	28.2-33.3	30.1
1-B	75-140	96	0.11- 7.87	4.06	7.52-9.36	8.44	28.3-31.8	29.6
2-S	67-107	81	2.21-12.45	6.91	7.38-9.28	8.44	28.0-34.9	30.3
2-B	74-110	89	1.69- 9.90	4.79	7.54-9.11	8.17	27.5-33.2	29.3
3-S	91-138	114	1.87-15.82	7.45	7.14-9.02	8.03	28.0-34.1	30.4
3-B	83-139	113	1.43-16.97	6.19	7.15-9.07	7.99	28.0-33.4	30.0

* S = 0.3 m below water surface, B = 0.3 m above bottom.

APPENDIX A: WATER QUALITY DATA

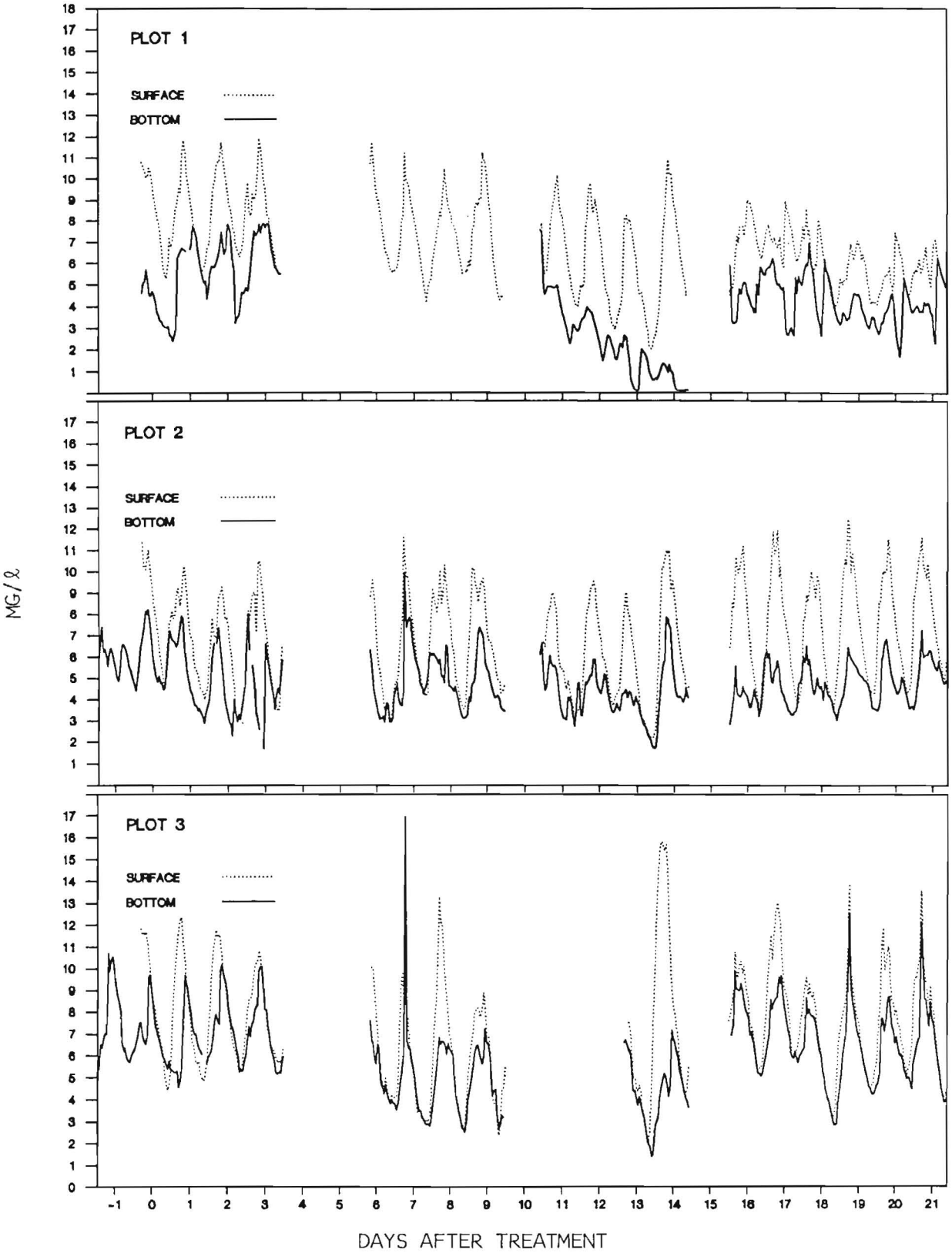

Figure A1. Dissolved oxygen concentrations of the water in the test plots

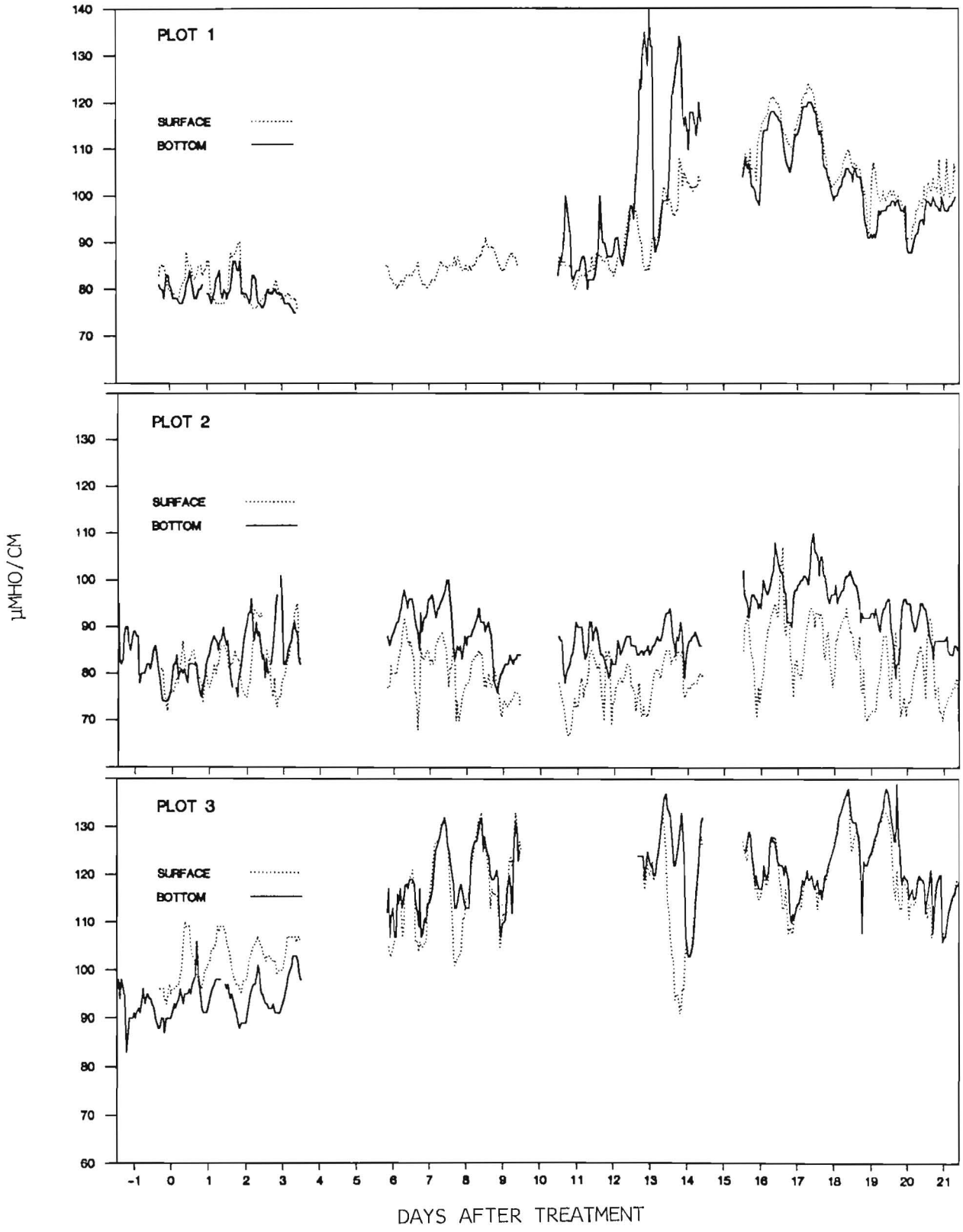

Figure A2. Specific conductance of the water in the test plots

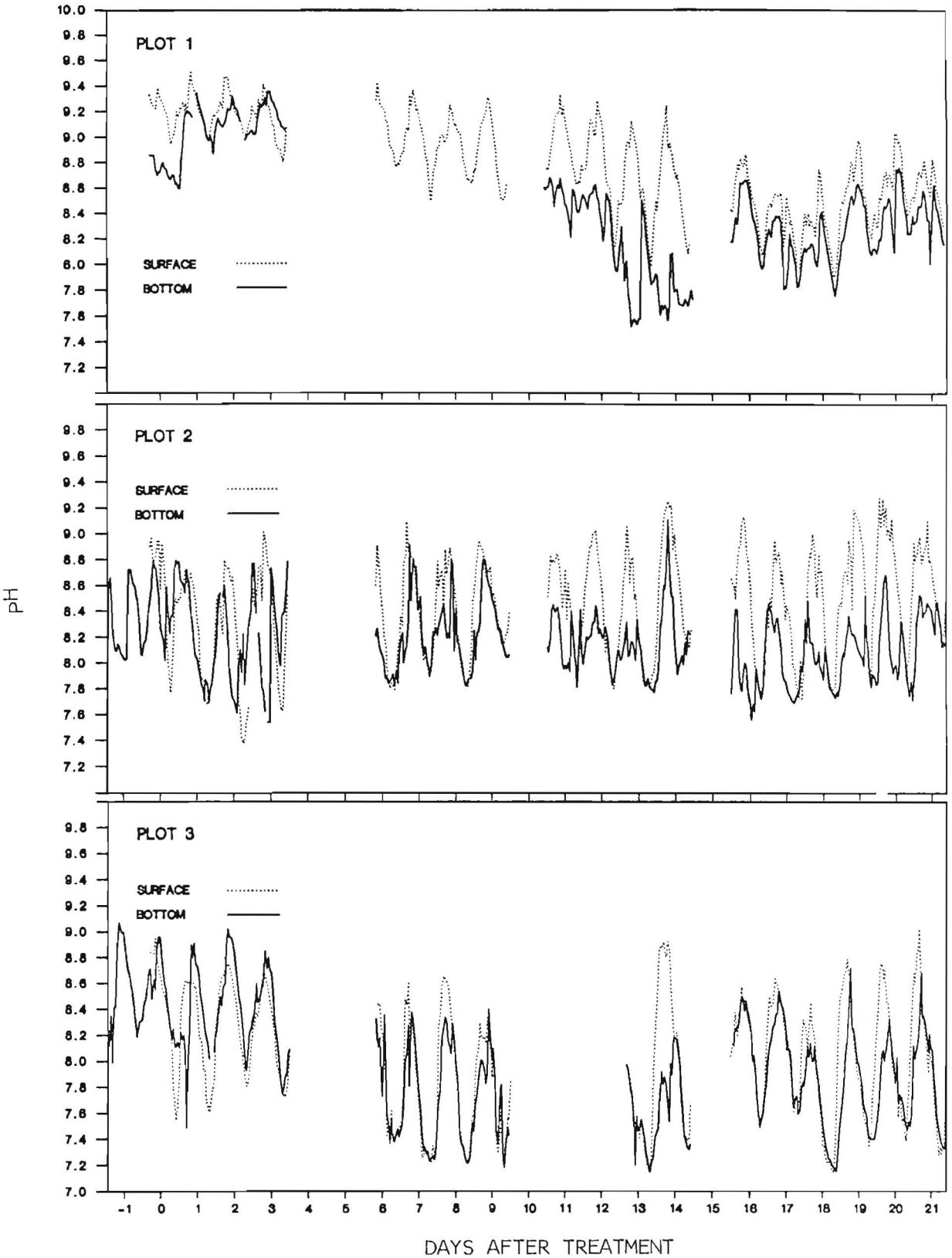

Figure A3. The pH of the water in the test plots

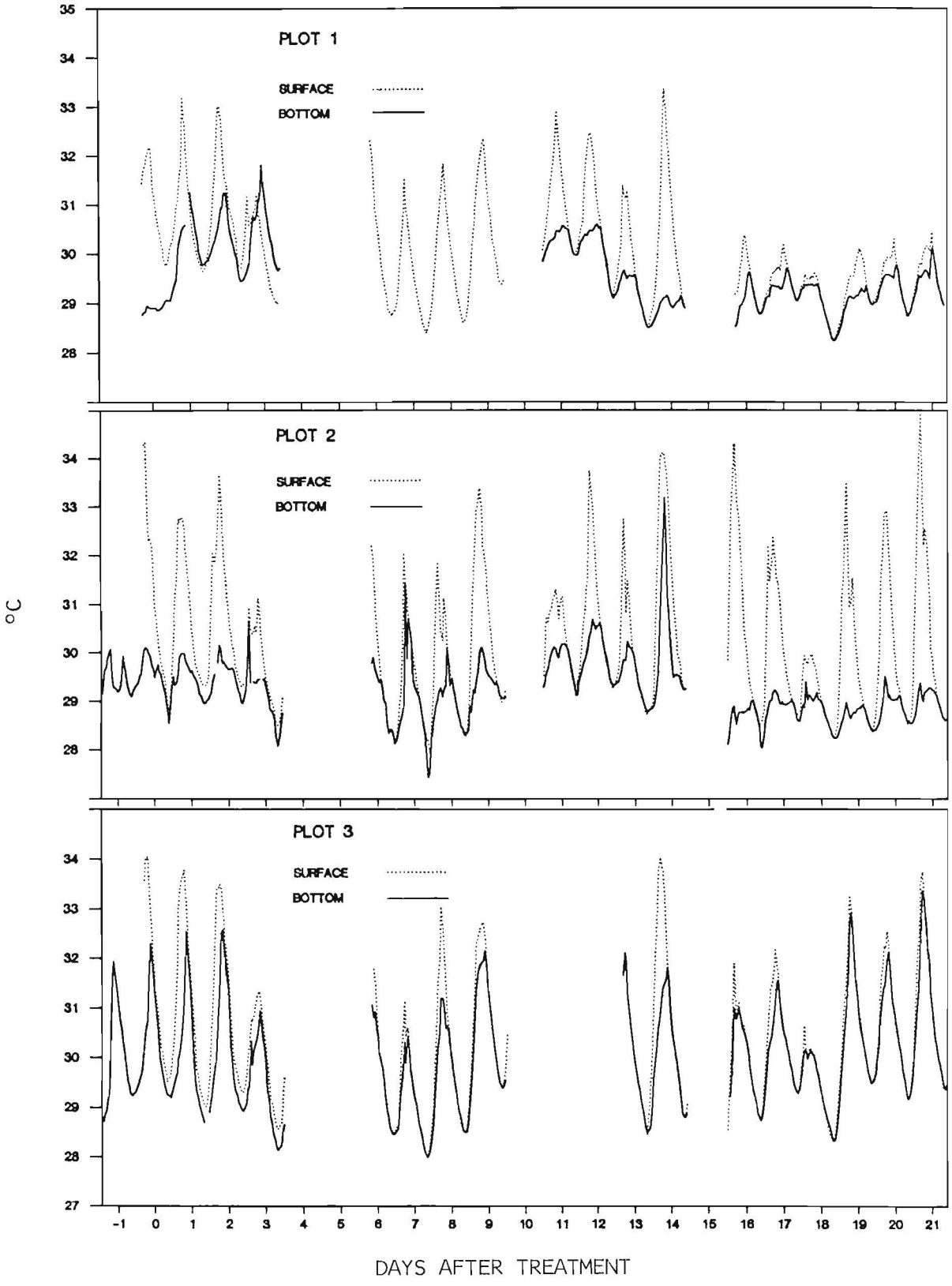

Figure A4. Water temperature in the test plots